



Description of EP0166980

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Method to the production of electrical conductive Homo and copolymers of pyrroles as well as their use the invention relates to a method to the production of electrical conductive by anodic Homo and copolymerization of the pyrroles in presence of Leitsalzen. The so obtained polymers according to invention are - generally filmförmige - materials, which possess an high electrical conductivity, an high mechanical level and favourable application technology properties.

From works of A.F. Diaz et al., J.C.S. Chem. one. COMM. 1979, side 635; J.C.S. Chem. one. COMM. 1979, side 854; ACS Org. Coat, plastic. Chem. one. 43 (1980) known became that become formed by anodic polymerization of pyrrole in presence of Leitsalzen films with electric conductivities up to  $10^2 \text{ } \Omega^{-1} \text{ cm}^{-1}$ . Here it concerns p-conductive polypyrroles, whereby mentioned as counterions above all  $\text{Bs}_4$ ,  $\text{Asz}_6$ ,  $\text{C}_{104}$  and  $\text{Xs}_504$  become. The mechanical properties of the so prepared films are however satisfactory by far not yet.

In accordance with the non-before-published European patent application 831058912 conductive Polypyrrol copolymers prepared can to become by anodic polymerization of pyrroles as well as other heterocycles, which a conjugated) t-Elektronensystem possess, which exhibit a significant higher mechanical level compared with the previously known electrical conductive polypyrroles. After another proposal können compounds from the class of the pyrroles with amino group contained aromatics such as aniline or phenylene diamine in presence by Leitsalzen to be copolymerisiert.

But also these Polypyrrol copolymers are still in need of improvement for particular application purposes.

Object of the instant invention is it to create a new other method to the production of polymers from the class of the pyrroles which possess a simultaneous high electrical conductivity and an high mechanical level and which opposite the known electrical conductive Polypyrrol systems exhibit an improved stability.

It was now found that this object becomes dissolved by a method, with which one compounds from the class of the pyrroles or mixtures of compounds of this class with other with pyrroles copolymerizable Compounds by anodic oxidation in polar electrolytic solution means in presence of Leitsalzen bottom separating polymers at the surface of the electrode of the polymerized.

The method is characterised in that one the polymerization in presence of Carbyndderivaten and of acidic ones with a current density from 0,1 to 20 m Amp/cm<sup>2</sup> accomplishes.

Subject matter of the invention are other particular arrangement forms of the method and the use of the polymers in accordance with the subsequent detailed description.

Bei by the invention process by anodic polymerization the produced polymers concerns it electrical high-leads itself zänige systems, which at least partly contain the anion of the Leitsalzen used with their production. One can call the polymers according to invention therefore also complexes from cations that polymers that pyrroles and Gegenanionen. Polymers of the invention beyond that an high mechanical level and an overall balanced and who good width unit characteristic picture, in particular also very good application schische properties, an excellent long term stability, which makes her eür the use in a very wide field of application suitable, possess.

Bottom compounds from the class of the pyrroles the unsubstituted pyrrole and the substituted pyrroles become, as the N-Alkylpyrrol in the frame of this invention > N-Arylpyrrole, those at the C-atoms monoalkyl or dialkyl-substituted pyrroles and those at the C-atoms #onohalogen or dihalogensubstituierten pyrroles understood. With the Bestellung copolymers according to invention the pyrroles can become alone or in mixture used with one another, so that the copolymers or an incorporated several various pyrroles can contain. Preferably the repeating Pyrrol units in the copolymers are derived essentially from unsubstituted pyrrole. Substitu ierte pyrroles become used with the production, for this the 3,4-Di alkylpyrrole, in particular such with 1 to 4 C-atoms in the alkyl radical, is like 3 - 4-Dimethylpyrrol and 3,4-Diethylpyrrol, like also the 3,4-Dihalogenpyrrole, in particular 3,4-Dichlorpyrrol, preferred.

To the production of copolymers of the compounds from the class of the pyrroles such compounds come into question, which result in from anodic oxidation of mixtures of pyrrole or pyrroles with these compounds copolymers, in whose molecules this Verbindungen-als Comono mer inheiten incorporated are. Suitable compounds, which result in the bottom indicated conditions with pyrrole or pyrroles of copolymers, e.g. are. Heterocycles with a konjugierten t-Elektronensystem. These are heteroaromatic compounds and become in the frame of this invention for the sake of simplicity also only as ~Heterocyden " referred. Preferably it acts with these heterocycles around 5 - or 6-gledrige of ring systems with or several, preferably one to three and in particular one or two heteroatoms, which can be if necessary, for example by alkyl groups, substituted at the heteroatom or at the ring carbon atoms. With the Heterocyden thereby preferably, just like with the pyrroles, at least two ring carbon atoms should be not substituted, in order to be able to accomplish the anodic oxidation simple and good. Examples for good suitable heterocycles are Furan, Thiophen, thiazole, Isoindol and derivatives, oxazole, thiadiazole, imidazole, pyridine, 3,5-Dimethylpyridin, pyrazine, 3,5-Dimethylpyrazin. Particularly

preserved has itself the 5-gliedrigen heterocycles, like Furan, Thiophen, thiazole and Thiadiazol. Die heterocycles can alone or into mixture to the use come with one another.

Other comonomers for pyrroles e.g. are. Amino group contained flavon IL electron system have. These aromatic compounds become referred in the frame of this invention for the sake of simplicity also only as "Aminoaromaten". Preferably it acts with this Aminoaromaten around 6-gliedrige or high-condensed ring systems with or several, preferably one to three amino group and if necessary one or two heteroatoms, which can be if necessary, for example by alkyl groups, substituted at the heteroatom or at the ring coal material atoms. With the "Aminoaromaten" thereby preferably, just like with the pyrroles, at least two ring Koh should be lenstoffatome not substituted, in order to be able to accomplish the anodic oxidation simple and good. Examples for good suitable comonomers are: Aniline, subst. Aniline such as p-phenacetin, p-Hethoxyanilin, 2-Aminoanilin or m-Aminoanilin, p-phenylene diamine, o-phenylene diamine > 2-Aminopyridin, Tetraamino benzene, p-Phenoxyanilin or m-Nitroanilin. The Aminoaromaten can come alone or into mixture with one another to the use.

Other comonomers e.g. are. Aminophenanthren, benzidine, Semidin, Aminochrysen, Aminocarbazol.

To the production of Pyrrol copolymers also nitrogenous acyl acid derivatives can, like e.g. as monomers. Acrylonitriles, Vinylcarbazol or vinyl of derivatives in particular Diaetonacrylamid, used become. Shown has itself that these acrylic acid or become to be able.

According to invention contain the copolymers beside the units from pyrroles recurring units from or the several Comonomer mentioned ren incorporated. In the copolymers the weight ratio of the units from pyrroles can vary to the units from the comonomers within wide limits, e.g. of 1: 99 to 99: 1. Preferably the weight ratio of these units in the copolymers amounts to 20: 80 to 90: 10.

The production of the Homo and copolymers of the compounds from the class of the pyrroles monomers, that are the pyrroles become and if necessary comonomers, in a polar electrolytic solution means in presence of a suitable Leitsalze anodic oxidized and polymerized.

The Gesamtmonomer Konzentration at monomers amounts to here generally about 0.1 to 1 mole per liter solvents. Since the anodic polymerization becomes usually only conducted up to small conversions, this concentration can be fallen below in addition, exceeded within wide limits.

As Leitsalze preferred ionic or ionizable compounds with anions strong, oxidative acidic ones serve or also of, if necessary with Nitro groups substituted aromatics with acidic groups. As cations for these Leitsalze in particular the alkali metal cations come, preferably Li<sup>+</sup> beside the alkaline earth metal cations and H<sup>+</sup>, > Na<sup>+</sup> or K<sup>+</sup>, in consideration very much favorable are also the NO<sup>+</sup> and NO<sup>2</sup>- cations as well as in particular the Onium cations, above all the nitrogen and the phosphorus, for instance the type R<sup>4</sup>N<sup>+</sup> and R<sup>4</sup>P<sup>+</sup>, where R hydrogen and/or low alkyl radicals C-atomen, preferably with 1 to 6, cyclo-aliphatic remainders, preferably with 6 to 14 C-atoms, or aromatic radicals, preferably with 6 to 14 C-atoms, it means. The bottom ammonium and Phosphonium cations are those particularly preferred, in those R hydrogen and/or an alkyl radical with 1 to 4 C-atoms represents. For preferred Onium cations in particular the Tetramethylumion, the Triethylumion is exemplary beside the NH<sup>4</sup>+ -ion > Tetra n butylammonium, the Triphenylphosphonium and the trichloroethylene n butylphosphonium cation the mentioned.

As anions for the Leitsalz BF<sub>4</sub><sup>-</sup>, Asz<sub>4</sub><sup>-</sup>, R-suction, on, proved SbF<sub>6</sub><sup>-</sup>, SbCl<sub>6</sub><sup>-</sup>, CmO<sub>4</sub><sup>-</sup>, ES<sub>04</sub><sup>-</sup> and S<sub>042</sub><sup>-</sup> as favorable. An other group from guidance salt anions, which become used with the invention process with particular advantage, are derived from aromatics with acidic groups. To it belong the C<sub>6</sub>E<sub>5</sub>COO<sup>-</sup>-Anion as well as in particular those Anions of if necessary with alkyl groups, mono, those or multiple substituted aromatic Sulfonsäuren. In of an other very favourable embodiment the aromatic nucleuses know acidic aromatics beside the acidic groups also still different substituents, in particular Nitro groups inertial. Among the acidic Nitroaromaten e.g. rank, the nitrophenols, the Nitrogruppen substituted aromatic carbonic acids and the Nitrogruppen substituted aromatic sulfonic acids. In particular the salts of Nitro, Dinitro, Trinitro benzoic acids as well as Nitro, Dinitro and trinitrobenzene-sulfone-acidic use find. Also the salts of Nitroaromaten with several acidic groups, like phenolic hydroxyl groups, are carboxyl groups and sulfonic acid groups suitable. Furthermore acidic aromatics with Nitrogruppen used can become. Paths of the good results achievable thereby Leitsalze with the benzene sulfone acid anion C<sub>6</sub>ES<sub>03</sub><sup>-</sup> or toluol sulfone acid anion CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>S<sub>03</sub><sup>-</sup> are whole particularly preferred.

The guidance salt concentration amounts to in the invention process generally 0.001 to 1, preferably 0.01 to 0.1 mole/liter.

The invention process becomes conducted in polar electrolytic solution means, which are able to loosen monomers and the Leitsalz.

If with water mixable organic solvents use find, a small amount at waters, generally up to 3 Ges.%, can become related to the organic solvent, added the Erhöhung of the electric conductivity, even if usually in an anhydrous system and in particular also without addition of alkaline making compounds one works. The solvents are protisch or aprotic. Particularly are suitable e.g. Acetone, acetonitrile, dimethylformamide, dimethyl sulfoxide, methylene chloride or Nisethylpyrrolidon.

After the start to the production of the electrical conductive Homo and copolymers the polymerization of the compounds becomes from the class of the pyrrole or the mixtures with other copolymer ion connections additional in presence of Carbonylderivaten and of acidic one conducted.

From the Carbonylderivaten are e.g. suitable. aliphatic or cyaloaliphatische Ketone such as acetone, methyl ethyl ketone, Cyclohexanon and their Homolo ge and halogen derivatives. Particularly suitable is aldehydes of heterocycles in the Pyrrolbionaldehyd and/or. Thiophencarbonaldehyd.

Also aldehydes come like aliphatische with at least 2 C-atoms, cyclo-aliphatic, heteroaromatic and aromatic aldehydes into question.

Suitable ones e.g. are. Acetaldehyd, acrolein, Propargylaldehyd, Cyclohexylcarboxaldehyd, Benzaldehyd, nitrobenzaldehyd, N-Dimethylaminbenzaldehyd, Thiophenaldehyd or Pyrrolaldehyd.

Also capped Carbonylderivate can become such as ketals, acetals or also Isooxazol used.

The Carbonyl derivative becomes used in such amounts that 0.1 to 1 mole Carbonyl derivative on 1 mole pyrrole and/or. a compound from the class of the pyrroles and/or. to 1 mole of the mixture to a compound of the class of pyrroles and another compound copolymerizable thereby are allotted.

Except the Carbonyl derivatives are present at the anodic oxidation of the pyrroles acidic ones. Suitable ones are z.B. organic acidic ones like aliphatic carboxylic acids e.g. Ant or acetic acid. Sulfonic acids such as toluene sulfonic acid or trifluoromethyl-sulfonic acid. Further inorganic acidic ones are suitable like borofluohydric acid, hydrogen fluoride, hydrochloric acid, sulfuric acid or phosphoric acid.

The acidic ones are in amounts from 0.1 to 50 Gew. - %, preferably from 1 to 25 Gew. - % in the electrolyte solutions contain.

At the method to the production that polymers from the class of the pyrroles preferred in a simple, usual electrolytic cell or electrolysis apparatus, existing from a cell without diaphragm, 2 electrodes and an external power source, one works. The electrodes can be thereby for example at the nickel, titania or from graphite; also precious metal electrodes, preferred platinum electrodes, can become used. Thereby it is favorable if at least the anode, in particular however both electrodes, laminar formed are. In a special arrangement form of the invention process the anode can become also from electrical conductive polymers a formed, like e.g. out by anodic oxidation prepared polypyrrole, doped, p-conductive polyacetylene or doped, broke that Polyphenylen. In this case the pyrroles and the Aminoaromaten become on generally film förmigen conductive polymers the up-polymerized.

Depending upon procedure guidance various types of Homo and copolymers can become obtained. One e.g. sets. , Then one receives a film förmiges polymer, which contains the monomer units in random division incorporated to precious metal electrodes and a mixture from pyrroles and the Aminoaromaten. The pyrroles and comonomers the cans in addition, stepwise, i.e. successively polymerized become. So one can polymerize beiseitsweise first only the pyrroles bottom deposition of a corresponding Polypyrrol film on the anode and up-polymerize subsequent by anodic oxidation comonomers these on the before generated polypyrrole. One receives in such a way "layered" constructed copolymers and/or. Copolymer films with high electrical conductivity.

This stepwise copolymerization can become natural also so made that one first comonomers and then the pyrroles the polymerized.

Except the mentioned simple electrolytic cell without diaphragm also different electrolysis mechanisms for the invention process use can find, for example cells with diaphragm or such with reference electrodes for exact potential regulation. To the control the layer-strong of the deposited films is a measurement of the amount of current (Amp/s) convenient.

Normally one accomplishes the polymerization with room temperature and bottom inert gases. Since the reaction temperature proved with the polymerization of the pyrroles as uncritical, the temperature can become however in a wide range varied, so long the solidification temperature and/or. Boiling temperature of the electrolytic solution means not under and/or. one exceeds. Generally a reaction temperature proved within the range of 0 to +50°C as very favourable.

As power source for the operation of the electrolytic cell, becomes conducted in which the invention process, each DC source is suitable, as e.g. a battery, which supplies a sufficient high electric voltage. The voltage appropriately lies within the range of approximately 1 to 25 volts; as particularly favourable voltages proved within the range of approximately 2 to 12 volts. The current density lies usually within the range of 0.1 to 20 mA/cm<sup>2</sup>.

During the electrolysis anodic deposited polymers according to invention washed become and with temperatures from 30 to 1500C, preferably bottom vacuum, dried the removal of adherent Leitsalz with solvents. With use of graphite, - precious metal or similar electrodes can be replaced thereafter the generally film förmig deposited copolymers easy of the electrode, above all if layer-strong over 50nm became deposited. If conductive, film förmige polymers become used as anode material, then become as mentioned, which are then find in accordance with used monomers on the polymere electrode material of up-polymerized, so that one receives a copolymer in this case, in which that as anode used polymers with incorporated.

The polymers according to invention show high electrical conductivities, generally within the range of 100 to 10<sup>2</sup>n cm<sup>-1</sup> and possess an high mechanical level. The measurement of the tearing strength and Reißfestigkeit films become from the copolymers according to invention with defined dimension (clamp-prolonged 25 mm, measuring length 10 mm, width 4 mm) stretched in accordance with DIN 53,504 on a INSTRON 1112-Maschine up to the breakage. The films skilled here only an insignificant elongation. The electric conductivity in -1 #-1 becomes certain by contact of the films with guidance silver and measurement according to the method of point of two. One receives identical results by measurement according to the method of point of four, whereby the transition resistances of the contact cannot play role. In addition the films have a favorable long term stability.

Polymers according to invention very good application technology properties could and to the production of electrodes, catalysts, electrical storage systems, preferably as electrodes for secondary batteries, as switch, semiconductor components, shielding materials, solar cells and to the antistatic equipment of plastics use find. Above all they lead there to a technical advancement, where an high mechanical level of the components is with small specific gravity and overall balanced properties of importance.

The invention becomes more near explained by the subsequent examples. The parts and percents relate indicated in the examples itself, if differently does not note, on the weight.

Example 1 6 parts pyrrole with 500 parts acetonitrile, 10 parts become konz.

Acetic acid, 1.5 parts 2-Pyrrolocarboxaldehyd and 1 part Tetrabutyl ammoniumphenylsulfonsäure mixed. This reaction solution flows through an electrolytic cell with a rotational speed of 1 l/h. The cell contains Platin-Elektroden of 1 mm of thickness. The current density amounts to 2 mA/cm<sup>2</sup> and their polymerization time amounts to 60 min. One works at a temperature of 250C. A black film is formed on the anode, which has a starch of approximate 55 µm. The weight of the film amounts to 1.2 parts.

After the washing of the film with water for the durations of 1 hour the film for the durations of 5 hours becomes with a temperature of 50-C and a pressure of 10#1 Torr dried. The electric conductivity of the film amounts to 30 S/cm.

The film can become with polyvalent metal ions gelatinized. For this purpose 1 cm<sup>2</sup> becomes large film pieces in metal solutions, which contain 10% metal salts in aqueous solution, stored. With use of Eisensulfat that amounts to Fe content of the film 12%. With use of cobalt nitrate solution 11.5 Z cobalt, with the use of chrome sulfate solution 14% chromium and with the use of Zinn-2-chloridlösung 5.2 X tin.

Example 2-10 it worked as in example 1, however in place of 2-Pyrrolcarbox aldehyde other Carbonylkomponenten like it in the table indicated are, used. The results obtained summarized in the table become.

Table 1 example Carbonyloleinat electric conductivity

No. Type amount S/cm

2 Isooxazol 2 35

3 p-nitrobenzaldehyde 3 40

4 p-Dimethylamino 3 30 benzaldehyd

5 acrolein 2 25

6 benzaldehyde 3 20

4 Thiophen-2-aldehyd 3 10

8 Zimtaldehyd 5 12

9 acetone 3 20

10 l-chlorine-acetone 4 16

11 Propargylaldehyd 3 5 example 12 one works as in example 1, however other acidic ones than acetic acid become used.

Table 2 example acidic electric conductivity

No. Type amount s/cm

12 formic acid 10 20

13 propionic acid 20 10

⚠ top14 tri fluorine methane 5 5 sulfone-acidic



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Claims of EP0166980

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Claims 1. Methods to the production of electrical conductive Homo and Copolymerisaten the pyrrole by anodic oxidation of compounds from the class of the pyrroles or of mixtures of compounds of these

Class with other compounds in polar organic solvents in presence of Leitsalzen, copolymerizable with pyrroles, more bottom

Separate polymers at the surface of the anode characterised in that one the polymerization in presence of Carbonylderivat and of acidic ones with a current density from 0,1 to 20 mAmp/cm<sup>2</sup> accomplishes.

2. Process according to claim 1, characterised in that one the Carbonyl of derivatives in amounts of 0,1 to 1 moles related to 1 mole of the compound from the class of the pyrroles or the mixtures with other compounds used copolymerizable with pyrroles.

3. Process according to claim 1, characterised in that one the acidic ones in amounts from 0,1 to 50 Gew. - Z related to the solution from electrolyte solvent and Leitsalz used.

4. Use from polymers, prepared after the method after Claim 1, as electrodes for primary and secondary batteries.

5. Use from polymers, prepared after the method after Claim 1, as conductors in electro-technology.